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ALKYLATION OF AROMATIC COMPOUNDS IN THE PRESENCE OF  $ZnCl_2$ .  
IV. CONDENSATION OF HALOGEN DERIVATIVES AND ALCOHOLS  
WITH AROMATIC COMPOUNDS UNDER PRESSURE

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Alkylated benzenes are regarded in the USSR as particularly val-  
 uable antiknock additives to aviation gasoline and are considered  
 superior to isoparaffins in that respect. Improved  
 methods for the synthesis of alkylated benzenes are described in this  
 article. It is possible that these methods are being considered as  
 an alternate way of synthesizing aromatic antiknock additives, or as  
 a supplementary method of synthesis to be applied to compensate for  
 inadequate yields or insufficient capacity limiting the usefulness of  
 some other method, such as aromatization, in the face of increased de-  
 mand.

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The initial article (1) of this series showed that this condensation pro-  
 ceeds only at sufficiently high temperatures (150-190 degrees). In experiments  
 with low-boiling components the reaction was conducted by gradually adding them  
 to melted  $ZnCl_2$  (1, 2). The favorable influence of an excess of HCl on the pro-  
 gress of the condensation has also been established.

The initial article noted in addition that, according to previously re-  
 ported research on the alkylation of benzene with alcohols in the presence of  
 $ZnCl_2$  in test tubes at 180-300 degrees, low yields of alkylbenzenes were obtained.

Only a few studies have been made of the use of  $ZnCl_2$  in alkylation: In  
 reactions of allylchloride with benzene (3),  $AlCl_3$ ,  $ZnCl_2$ , and  $FeCl_3$  have been  
 used as catalysts,  $FeCl_3$  proving to be the best. The condensation of secondary  
 butylbromide with 3-methyl-4-chlorophenol in the presence of  $ZnCl_2$  has been des-  
 cribed (4). A recent study (5) characterized  $ZnCl_2$  (rather than  $AlCl_3$ , which  
 leads to the formation of numerous by-products) as the better catalyst in the

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condensation of tertiary butylchloride with naphthalene and tetralene, the reaction in this case proceeding at 90-100 degrees and giving 30-33 percent of the theoretical yield of butylnaphthalene and butyltetralene. Various patents (6) are based on the use of  $ZnCl_2$  either by itself or in combination with  $AlCl_3$  for the condensation of aromatic compounds in the alkyl halides. More research and patents have been concerned with the alkylation of aromatic compounds by olefins in the presence of  $ZnCl_2$ , e.g., Isagulyants and Bagryantseva (7) prepared butylphenol from phenol and isobutylene as well as from phenol and isobutylene as well as from phenol and tertiary butylchloride.

For this paper, the condensation of n.-butylchloride with benzene, toluene, naphthalene, and phenol was studied; and several experiments with isamylchloride and ethylbromide were carried out as well.

The reactions were conducted in a steel bomb with a capacity of approximately 100 milliliters at 170-250 degrees. At first, a large quantity of  $ZnCl_2$  was used (0.5-0.82 gram-mol); later it was found, in conformity with earlier published data (8), that 0.1-0.2 gram-mol is sufficient.

In experiments with n.-butylchloride and isoamylchloride, about 80 percent of the theoretical yield of monalkyl derivatives was prepared; with naphthalene the yield was somewhat lower (60-70 percent). Condensation with ethylbromide gave only 40-50 percent of the theoretical yield of monalkyl derivatives and many products with high boiling points.

To clarify the role of  $ZnCl_2$  in the above reactions, several experiments were carried out at lower temperatures (100-150 percent) in ordinary glass apparatus and not under pressure. In all such cases a very low yield of the alkyl derivatives was obtained; from this it was concluded that the mechanism of condensation in the presence of  $ZnCl_2$  is different from that in the presence of  $AlCl_3$ . Apparently, high temperatures are necessary for the formation of active intermediate products (possibly, olefins). The attempt to carry out the condensation by heating n.-butylchloride with toluene in the bomb at 260 degrees without  $ZnCl_2$  failed to produce even traces of alkylbenzenes. The catalytic role of  $ZnCl_2$  at high temperature and pressures is therefore apparent.

The condensations of n.-butyl, isopropyl, and ethyl alcohols with benzene and toluene under pressure were studied. These experiments were conducted by heating the alcohol in the bomb which was saturated with HCl, and contained benzene (or toluene) and  $ZnCl_2$ . With ethyl alcohol, the reaction proceeded only at about 300 degrees, the yield being low, and in this case many polyalkylbenzenes were formed. With the other two alcohols, the condensation proceeded smoothly at 220-230 degrees, giving yields of 75-80 percent -- higher than those obtained without pressure (1) (50-70 percent). In these experiments it was also discovered that the amounts of  $ZnCl_2$  used can be very small 3. e.g., 0.1 gram-mol and even 0.02 gram-mol in one gram-mol of alcohol gave about 75 percent of the theoretical yield of butyltoluene. An attempt to carry out the condensation without using the catalyst by prolonged heating of a mixture of alcohol, saturated with HCl, and toluene at 250 degrees in the bomb produced only negative results.

It was noted that the condensation of n.-butyl alcohol with benzene and toluene in the presence of  $AlCl_3$  gives poorer results, owing to the cleavage of the alcohol (9). Investigation of the products of condensation of benzene with n.-butyl alcohol and n.-butylchloride by preparing acetamino derivatives (10) showed that secondary butylbenzene was formed; such isomerization of the radical confirms the hypothesis concerning the intermediate formation of olefins during condensation.

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